

The University of Chicago

HYDROGEN COMPOUNDS OF ARSENIC

A PART OF A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By
ALPHONSE PECHUKAS

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Hydrogen Compounds of Arsenic. I. Preparation of Arsine in Liquid Ammonia. Some Physical Properties of Arsine

BY ALPHONSE PECHUKAS

Due to the success in the preparation of the hydrogen compounds of germanium¹ and silicon² in liquid ammonia by the action of ammonium salts on magnesium germanides and silicides, respectively, an analogous method was chosen for the preparation of large amounts of arsine required for extensive investigations in this Laboratory. The liquid ammonia method gives high yields of arsine, eliminates objectionable impurities found in the aqueous method and does not

produce any other hydrogen compounds of arsenic. In view of the conflicting data in the literature, it appeared advisable to redetermine some of the physical properties of arsine so as to have a control of the purity of the gas to be used in later studies.

Preparation of Arsine.—The arsine was prepared by treating sodium arsenides³ with ammonium bromide in liquid ammonia by a procedure analogous to that previously described for the preparation of germanes and

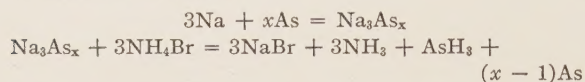
(1) Kraus and Carney, *J. Am. Chem. Soc.*, **56**, 765 (1934).

(2) Johnson and Isenberg, *ibid.*, **57**, 1349 (1935).

(3) Magnesium arsenides were found to give poor yields of arsine; not greater than 25%.

silanes.^{1,2} The sodium arsenides were prepared by allowing a solution of sodium in liquid ammonia to react with freshly sublimed arsenic. Since an excess of arsenic was used, polyarsenides were undoubtedly present in addition to the normal arsenide, Na_3As .⁴

The reactions involved in the preparation of arsine may be expressed as follows



The liberated gases, arsine and hydrogen, were collected over water to remove ammonia, dried over phosphorus pentoxide, and then fractionally distilled at low pressure at -112° after the hydrogen had been removed by the pumps. The molecular weight of the gas was calculated from vapor density determinations on several samples and was found to range from 77.6 to 77.9 (calculated value for arsine is 77.9). The yield of arsine based upon the

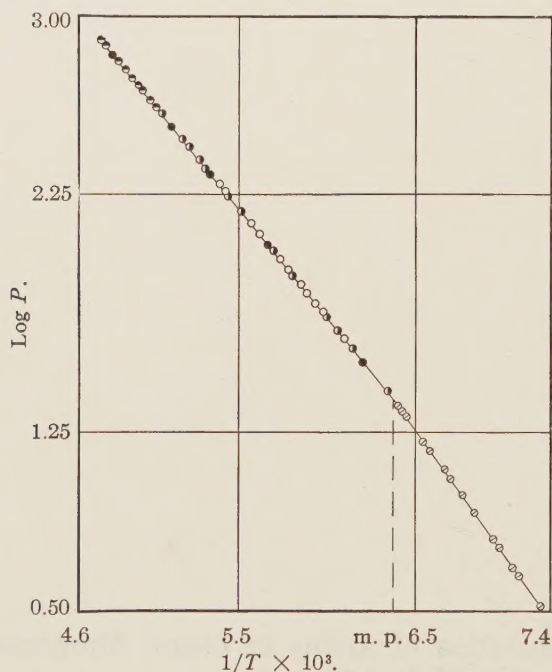


Fig. 1.—Vapor tension of liquid and solid arsine.

amount of sodium initially combined with arsenic was found to range from 60 to 90%. Arsine was the only gas liberated found to contain arsenic. In addition, no arsenic-hydrogen compound remained in the reaction tube after the ammonia had been allowed to evaporate. Evidence for this fact was obtained by heating the residue in the reaction tube to 300° . Since hydrogen was not liberated in this treatment it may be assumed that no solid hydrogen compounds of arsenic were present.

(4) Hugot [*Compt. rend.*, **129**, 603 (1899)] describes the normal alkali metal arsenides as brick-red in color, and a polyarsenide of the composition $\text{K}_2\text{As}_4\text{NH}_3$ as orange. In the present work, both the red and orange solids were observed in every experiment. Zintl, Goubeau and Dullenkopf [*Z. physik. Chem.*, **154**, 1 (1931)] have found Na_3As , Na_3As_2 , Na_3As_3 and Na_3As_7 to exist in ammonia solutions. They show a relatively low solubility in ammonia and undoubtedly separate from solution with ammonia of crystallization.

Vapor Tension of Liquid and Solid Arsine.—Arsine, obtained by the method described above, is a colorless gas which condenses to a water-clear liquid and freezes to a white crystalline solid.⁵ To determine the vapor tension a purified sample of arsine of molecular weight 77.8 was used. The arsine was condensed into a small bulb connected to a mercury manometer. The volume of the entire system was about 22 cc. The bulb was surrounded by constant temperature baths consisting of solid chloroform, ethyl acetate, isopropyl acetate and carbon disulfide in equilibrium with their respective liquids. The liquids from which these baths were prepared were not purified since their freezing points were not used as standards, but merely as a means of maintaining a constant temperature over a reasonably long period of time. The temperature of each bath was determined by a vapor tension thermometer.⁶

As a check upon the fixed point measurements a solution of alcohol in ether was cooled to -120° with liquid nitrogen and was then placed about the arsine bulb and allowed to warm slowly. Readings of the vapor tension were taken at convenient temperature intervals. The temperature was determined either with calibrated vapor tension thermometers or with a copper-constantan thermocouple which had been standardized against the thermometers. A Leeds and Northrup Type K potentiometer was employed in the measurement of the thermocouple potentials. The vapor tensions determined in this manner are plotted in Fig. 1 as $\log p$ against $1/T$ and are found to be in good agreement with the fixed point values.⁷

The results show the normal boiling point of arsine to be -62.4° .^{8,9} The heat of vaporization is calculated to be 416 cal./mole and Trouton's constant, 19.8 cal./mole/degree. Durrant, Pearson and Robinson⁹ give 434 cal./mole for the heat of vaporization at the boiling point and a value of 20.26 for Trouton's constant.

The melting point of arsine was determined by a method described by Stock.¹⁰ An ethylene vapor tension thermometer was used for the temperature measurements. Five determinations gave the following values for the melting point: -116.3 , -116.5 , -116.2 , -116.3 , -116.3° . From these values -116.3° may be taken as the melting point. Durrant, Pearson and Robinson give -111.2° for the melting point of arsine.

The vapor tension of solid arsine was determined at a series of temperatures by condensing the gas in a small

(5) Natta and Casazza [*Gazz. chim. ital.*, **60**, 851 (1930)] have studied the crystal structure of solid arsine.

(6) A carbon dioxide vapor tension thermometer was used for the range, -112 to -78° , while an ammonia thermometer was used for the range, -74 to -60° .

(7) The vapor tension values obtained with the use of the fixed point baths are indicated in Fig. 1 by solid black circles; those obtained with the carbon dioxide vapor tension thermometer, by solid white circles; with the ammonia vapor tension thermometer, by horizontal half circles; with the copper-constantan thermocouple, by vertical half circles; and the crossed circles represent values for solid arsine obtained with the aid of an ethylene vapor tension thermometer.

(8) Values for the boiling point of arsine ranging from -40 to -70° have been reported in the literature. See Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. IX, p. 53.

(9) Recent work by Durrant, Pearson and Robinson [*J. Chem. Soc.*, **730** (1934)] shows a value of -58.5° for the boiling point of arsine.

(10) Stock, *Ber.*, **50**, 156 (1917).

TABLE I
 VAPOR TENSION OF SOLID AND LIQUID ARSINE

Temp., °C.	-138.0	-135.3	-134.0	-133.1	-132.0	-131.2	-129.0	-127.0	-124.5
Press., mm.	2.0	3.0	3.7	4.05	4.5	4.95	6.4	8.1	10.9
Temp., °C.	-123.0	-121.2	-120.2	-119.0	-116.7	-116.1	-115.4	-112.5	-111.9
Press., mm.	12.4	14.7	16.1	18.5	22.8	25.0	27.0	33.7	35.0
Temp., °C.	-111.0	-110.2	-109.0	-108.3	-106.3	-104.3	-103.3	-102.2	-100.8
Press., mm.	40.0	42.3	44.1	47.4	54.0	62.8	68.5	74.7	80.7
Temp., °C.	-99.7	-98.7	-97.5	-96.6	-95.8	-94.8	-93.7	-92.7	-92.0
Press., mm.	88.5	95.3	103.5	109	113	124	134	148	151
Temp., °C.	-90.7	-89.4	-88.7	-87.7	-86.6	-85.7	-84.3	-83.5	-81.8
Press., mm.	164	177	184	198	213	219	246	257	283
Temp., °C.	-79.9	-78.9	-77.5	-76.6	-75.4	-74.3	-73.6	-72.2	-71.1
Press., mm.	316	330	350	370	397.5	419	432	467	496
Temp., °C.	-70.0	-68.8	-68.0	-66.9	-65.6	-64.3	-62.8		
Press., mm.	523	556	577	613	647	694	734		

bulb connected to a short mercury manometer of wide bore, and placing an alcohol-ether bath at -140° around the solid. The bath was then allowed to warm slowly and the vapor tension was read on the manometer with the aid of a precision cathetometer reading to 0.04 mm. The temperature was determined with an ethylene vapor tension thermometer. The results for the solid are also plotted in Fig. 1. A straight line plot is obtained which is found to intersect the line for liquid arsine at the melting point, -116.3° . This is a good confirmation of the melting point obtained in the direct determination. The heat of sublimation calculated from the slope of the $\log p-1/T$ plot is 484_0 cal./mole. The heat of fusion of the solid is therefore 67_5 cal./mole. The vapor tension at the triple point has a value of 24.4 mm. The equation for the vapor tension of the liquid is

$$\log_{10} p_{\text{mm.}} = -(910.6/T) + 7.198$$

while that for the solid is

$$\log_{10} p_{\text{mm.}} = -(1057/T) + 8.141$$

Table I gives the vapor tension values for both the solid and liquid arsine.

The Density of Liquid Arsine.—Using a pycnometer consisting of a small bulb with a capillary stem, the density of liquid arsine was determined by comparison with the density of liquid ammonia. Values for the latter have been determined accurately.¹¹ Ammonia which had been dried thoroughly over metallic sodium was distilled into the bulb and maintained at constant temperature by means of a well-stirred bath of solid chloroform in equilibrium with its liquid in a transparent Dewar vessel. The level of the liquid in the capillary stem of the pycnometer was determined with respect to a reference mark with the aid of a cathetometer. The ammonia was allowed to evaporate into a known volume after the cooling bath had been removed and the pressure of the ammonia gas was then determined. In this manner, the volume, and therefore the weight, of the gaseous ammonia could be calculated assuming the gas to obey the perfect gas laws. After correcting for the amount of ammonia vapor above

the liquid in the pycnometer (about 2 mg.), the weight of liquid ammonia was obtained. With the density of liquid ammonia known, the volume of the pycnometer to the reference point on the stem could be determined readily. The volume so obtained was 0.849 ± 0.002 cc.

The ammonia was then replaced by arsine and the same procedure was employed to determine the density of the latter. Constant temperature baths corresponding to those used in the vapor tension measurements likewise were employed. The measurements were made at several temperatures ranging from -64 to -112° . The values given in Table II represent the average of not less than four, nor more than seven, determinations at each temperature.

TABLE II

DENSITY OF LIQUID ARSINE AT DIFFERENT TEMPERATURES

Temp., °C.	-64.3	-76.9	-85.4	-96.0	-111.8
Density, g./cc.	1.640	1.670	1.692	1.723	1.766
Deviation, g./cc.	0.001	0.002	0.002	0.006	0.001

A plot of the density of liquid arsine against the temperature gives a smooth curve, the equation for which may be expressed as

$$d = 1.516 - 0.00150t + 0.00000663t^2$$

where d is the density in g./cc. and t , the temperature in $^{\circ}\text{C}$. From this equation the density of arsine at the normal boiling point, -62.4° , is found to be 1.635 g./cc. Extrapolating to -60° , the density is 1.629 g./cc., which value is in substantial agreement with that obtained by Durrant, Pearson and Robinson,⁹ who have reported a value of 1.625 g./cc. at this temperature.

Solubility of Arsine in Liquid Ammonia.—An attempt was made to determine the solubility of arsine in liquid ammonia through a study of the pressure-composition relationships for the two-component system. However, considerable difficulty was found in establishing equilibrium conditions and, in addition, the arsine was observed to be only slightly soluble. Qualitative measurements indicated the solubility of liquid arsine in liquid ammonia to be less than 1%. The saturated solution appears yellow in color, even at temperatures as low as

(11) Cragoe and Harper, *Sci. Papers of the Bur. of Stand.*, No. 420, p. 313 (1921).

-80° , and according to its chemical behavior the arsine must be appreciably ionized.¹²

We wish to acknowledge the aid of a grant from the National Research Council for the liquid nitrogen used in this study.

Summary

Arsine has been prepared in good yields by the action of ammonium bromide on sodium arsenides

(12) In connection with this problem a rapid method of separation and determination of arsine in an arsine-ammonia gas mixture was found. Ammonia may be removed quantitatively from a mixture of the two gases without loss of arsine by liquefying the mixed gases on anhydrous calcium chloride which has been previously heated in a vacuum to 400° . The ammonia combines with the calcium chloride to form a solid ammonate but the arsine does not produce a similar combination possessing any appreciable stability at temperatures as low as -78° . If the calcium chloride and its ammonate are kept at this temperature, the arsine may be distilled into a suitable container and condensed at the temperature of liquid nitrogen. Two such treatments were found to remove the ammonia quantitatively from 200 cc. of a mixture of the gases containing 90% ammonia by volume, without loss of arsine.

in liquid ammonia. Arsine was found to be the only arsenic containing gas liberated in the reaction. No solid arsenic hydrogen compounds are formed.

The vapor tension of solid and liquid arsine has been determined over a considerable range of temperature. From the measurements the boiling point has been found to be -62.4° ; the melting point, -116.3° ; the heat of vaporization, 416₅ cal./mole; the heat of sublimation, 484₀ cal./mole; and the heat of fusion, 67₅ cal./mole.

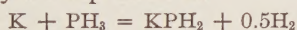
The density of liquid arsine has been determined at temperatures ranging from the melting point to the boiling point.

Liquid arsine is only slightly soluble in liquid ammonia.

Hydrogen Compounds of Arsenic. II. Sodium and Potassium Dihydrogen Arsenides

BY ALPHONSE PECHUKAS

Ammonia is known to exhibit some acidic properties since it conducts electricity to an appreciable extent and reacts with strongly electropositive metals to form dihydrogen nitrides (amides). Joannis¹ has shown that phosphine reacts with the common alkali metals in liquid ammonia to produce dihydrogen phosphides (phosphamides). In the case of potassium the reaction may be expressed as



Since arsenic shows a greater tendency than phosphorus to become electropositive one would expect the arsenic-hydrogen bonds of arsine to be weaker than the phosphorus-hydrogen bonds of phosphine. If the reaction between the alkali and alkaline earth metals and the hydrogen compounds of the fifth group elements is dependent upon the lability of the hydrogen atoms, arsine would be expected to react with these metals more readily than does phosphine and, in turn, ammonia. Gay-Lussac and Thenard² observed that hydrogen is liberated from arsine when the latter is treated with sodium or potassium and that the arsenic probably enters into combination with the metal. Lebeau³ investigated this reaction fur-

ther, both with the pure alkali or alkaline earth metals and their liquid ammonia solutions. He prepared calcium arsenide (Ca_3As_2) by the action of liquid arsine on solid calcium; in liquid ammonia solution arsine was found to react with calcium rapidly to give a yellow compound which decomposes at 150° to produce a brown arsenide of calcium. Using sodium instead of calcium, he obtained a bright yellow solution when arsine was passed into a liquid ammonia solution of the metal. Evaporation of this solution produced a red solid to which Lebeau ascribed the composition $\text{Na}_3\text{As}(\text{NH}_3)_x$.

Since arsine is appreciably soluble in liquid ammonia⁴ and appears to be somewhat ionized in this medium, it appeared advisable to prepare some of the alkali metal salts and study the chemistry of these substances.

The Reaction of Arsine with Sodium and Potassium.—Gaseous arsine, of known purity,⁴ was passed into a solution containing a weighed amount of sodium or potassium in liquid ammonia at -78° . The type of apparatus used has been described elsewhere.⁵ The arsine was found to react very rapidly with the ammonia solution of the metal, changing the color of the latter from

(1) Joannis, *Compt. rend.*, **119**, 557 (1894).

(2) Gay-Lussac and Thenard, *Ann. chim. phys.*, [1] **73**, 229 (1810).

(3) Lebeau, *Bull. soc. chim.*, [3] **23**, 251, 340 (1900); *Ann. chim. phys.*, [7] **25**, 470 (1902).

(4) Johnson and Pechukas, *J. Am. Chem. Soc.*, **59**, 2065 (1937).

(5) Kraus and Brown, *ibid.*, **52**, 4031 (1930).

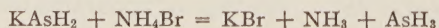
the characteristic blue to green and finally to a brilliant yellow. The disappearance of the blue color was used as an indicator for the completion of the reaction. Hydrogen was liberated in the reaction and was separated from the unreacted arsine and identified by its vapor density and failure to condense at liquid nitrogen temperatures (mol. wt. found, 4.8, 4.5). The metal dihydrogen arsenide appeared to be appreciably soluble in liquid ammonia, producing a bright yellow color.

After the ammonia had been removed from the reaction mixture by evaporation, a very pale yellow, almost white, solid was left crystallized on the walls of the reaction vessel. The solid salt does not contain any ammonia of crystallization at room temperature since in every experiment the weight of the product was found to correspond to the sum of the weights of the alkali metal and arsine used. In one instance the solid was allowed to stand for sixty hours *in vacuo* at room temperature and was found to remain unchanged. No change in weight was observed and when redissolved in ammonia at -33° the solution of the salt behaved chemically as though freshly prepared. Evidently, the salt is not ammonolyzed in solution at temperatures as high as -33° . When the salt is exposed to air a vigorous reaction takes place with the liberation of considerable heat and the deposition of a brown solid, presumably arsenic and solid arsenic-hydrogen compounds. Data for the preparation of the sodium and potassium dihydrogen arsenides are given in Table I. The following equation expresses the course of the reaction



where M represents either sodium or potassium.

The Action of Ammonium Bromide on Potassium Dihydrogen Arsenide.—Additional evidence for the composition of potassium dihydrogen arsenide was obtained by treating an ammonia solution of the salt with ammonium bromide, which behaves as an acid in this medium. A condensable gas was liberated in the reaction and was found to be arsine. It was separated from ammonia by treatment with calcium chloride⁴ and identified by its vapor density. The results are recorded in Table II and conform to a reaction which may be expressed by the equation



Column 1, Table II, refers to the weight of potassium used in the preparation of KAsH_2 . The amount of arsine liberated in the reaction and subsequently collected was found to be about 90–95% of the theoretical amount. This difference is probably due in part to a loss involved in the

TABLE I
THE PREPARATION OF SODIUM AND POTASSIUM DIHYDROGEN ARSENIDES⁶

Metal used, g.	Arsine used, cc.	H ₂ obtained, cc.	Molar ratio M: AsH ₃ : H ₂
Sodium			
0.139	144.0		1:1.00
.357	346.7		1:1.00
.216	214.0	112.8	1:1.00:0.54
Potassium			
0.0482	24.1	11.9	1:0.87:0.43
.0873	47.3	24.2	1:0.95:0.48
.133	74.7	36.7	1:0.98:0.49
.160	93.0	47.0	1:0.99:0.50
.175	102.7	49.7	1:1.00:0.49
.188	107.8	54.5	1:0.99:0.50
.224	127.2	65.2	1:1.00:0.51
.237	138.1	68.9	1:1.02:0.51

collection of the arsine over water; in addition, it is difficult to recover small amounts of the gas quantitatively.

TABLE II
ACTION OF NH_4Br ON KAsH_2 IN LIQUID AMMONIA

Wt. K, g.	Mol. wt. of gas	AsH ₃ (found), cc.	AsH ₃ (calcd.) cc.
0.174	78.6	75.8	79.3
.0742		34.9	38.8
.0482	78.4	20.7	24.1
.0873		43.1	47.3

The Action of Potassium Amide on Arsine.—An amount, 0.118 g., of metallic potassium was dissolved in liquid ammonia containing a few mg. of ferric nitrate as a catalyst for the formation of potassium amide. The solution of the latter at -78° was treated with an excess of arsine gas with the formation of a yellow solution characteristic of potassium dihydrogen arsenide. An amount, 66.9 cc., of arsine was consumed in the reaction; thus 3.05 millimoles of potassium converted to the amide required 2.95 millimoles of arsine. Evidently, the reaction is



The Action of Methyl Chloride on Potassium Dihydrogen Arsenide.—To further substantiate the composition of potassium dihydrogen arsenide and to obtain some information relative to its chemistry, the salt was treated with methyl chloride in liquid ammonia at -78° . As an illustrative experiment, 0.1083 g. (2.69 millimoles) of potassium was treated with 66.4 cc. (2.96 millimoles) of arsine and the excess arsine was removed by fractional distillation. The yellow solution of the salt so obtained was treated with 62.4 cc. (2.79 millimoles) of methyl chloride and a white precipitate appeared in the liquid ammonia as its yellow color faded. After the volatile products of the reaction had been removed by evaporation, the residue left in the reaction flask was analyzed for chloride ion, which was found to be present. The residue was dissolved in water, with the formation of a clear solution, and after the hydrogen ion concentration had been adjusted with dilute nitric acid, standard silver nitrate solution was added

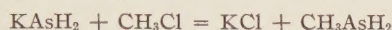
(6) Experiments with sodium and arsine were performed by Dr. A. E. Sidwell of this Laboratory.

TABLE III

VAPOR TENSION OF METHYLARSINE

Temp., °C.	-74.0	-71.7	-69.3	-66.8	-64.8	-62.8	-60.2	-58.0	-56.0	-54.2	-51.5
Press., mm.	18.2	21.1	24.1	28.5	33.0	37.1	43.7	49.9	55.3	63.0	71.7
Temp., °C.	-49.6	-46.5	-44.4	-42.2	-40.6	-38.4	-36.1	-33.3	-31.6	-29.2	-27.1
Press., mm.	80.0	94.7	105	119	127	143	158	182	198	220	242
Temp., °C.	-24.8	-22.5	-21.0	-19.0	-17.1	-16.1	-15.2	-13.6	-12.3	-11.0	-9.8
Press., mm.	268	294	313	338	364	381	397	418	442	468	496
Temp., °C.	-8.6	-6.9	-5.8	-4.2	-2.3	-1.0	0.0	1.8	3.0		
Press., mm.	520	544	578	606	657	687	709	753	781		

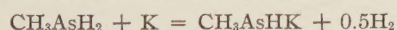
until the dichlorofluorescein indicator end-point was reached. The solution so prepared required 26.36 cc. of 0.0990 *N* silver nitrate solution, corresponding to 2.61 millimoles of potassium chloride in the original solution. Evidently, a reaction occurs between potassium dihydrogen arsenide and methyl chloride leading to the formation of an almost quantitative amount of potassium chloride. The yield of methylarsine was found to range from 70 to 80% based on the equation



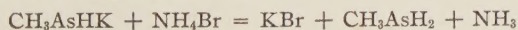
Evaporation of the liquid ammonia solution liberated large quantities of ammonia, a small amount of methylarsine and the unreacted methyl chloride. Most of the ammonia was removed by passing the mixture through water. The residual gases were dried in the vacuum system with phosphorus pentoxide and were then subjected to fractional distillation. Methylarsine was identified by its molecular weight determined by the vapor density method (found: 91.0, 93.0, 93.9, 93.1, 93.2; calcd. for CH_3AsH_2 , 92.0).

Vapor Tension of Methylarsine.—The vapor tension of liquid methylarsine was determined over a range of temperature, -74 to $+3^\circ$. Standardized ammonia and pentane vapor tension thermometers were used for the temperature measurements. The normal boiling point of the substance was found to be 2.0° , which value corresponds very closely to that reported by Dehn⁷ (2° at 755 mm.). The heat of vaporization was calculated from the vapor tension data and found to be 539₀ cal./mole. The melting point was found to be -143° by the method of Stock.⁸ The vapor tension data are given in Table III.

Methylarsine and Potassium.—A small amount of metallic potassium, 0.1372 g. (3.5 millimoles), was dissolved in liquid ammonia at -78° and methylarsine was passed into the solution until the blue color was discharged. For this process 77.4 cc. or 3.45 millimoles of methylarsine was required. Hydrogen gas, 39.4 cc. (1.75 millimoles), was liberated in the reaction. It was collected by means of a Toepler pump and its vapor density was determined (mol. wt. found, 3.8). The resulting ammonia solution appeared orange in color. Evidently methylarsine reacts with metallic potassium in liquid ammonia as follows



Addition of ammonium bromide regenerates methylarsine from the potassium salt.



The molecular weight of the methylarsine formed in the

reaction was determined by the vapor density method (found, 92.3; calcd. for CH_3AsH_2 , 92.0). The physical and chemical properties of the potassium salt of methylarsine will be described in a later communication.

Thermal Decomposition of Potassium Dihydrogen Arsenide.—Potassium dihydrogen arsenide is thermally stable at room temperature. When heated it shows no evidence of decomposition below 115° . At this temperature it begins to darken, becoming brown in color, with the liberation of a gas. This gas was forced over mercury with a Toepler pump, its volume was measured and it was identified as hydrogen by its molecular weight (found, 2.5, 2.3, 2.2). Decomposition of the solid may be completed by heating to 175° . The residue appears blue-black in color. Data for the decomposition of the arsenide are given in Table IV. Column one represents the amount of potassium used in the preparation of KAsH_2 . The calculated volume of hydrogen given in the third column is taken as twice the volume of hydrogen liberated in the preparation of KAsH_2 . The results show that one mole of hydrogen gas is liberated for every mole of KAsH_2 subjected to decomposition. The reaction may be expressed by the equation

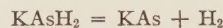


TABLE IV

THERMAL DECOMPOSITION OF POTASSIUM DIHYDROGEN

Wt. K, g.	ARSENIDE	
	H ₂ (found), cc.	H ₂ (calcd.), cc.
0.1032	55.6	56.4
.1858	101.0	103.0
.1884	104.0	109.0
.1186	64.6	66.8
.1142	61.7	63.4
.0869	47.2	49.8
.2244	121.5	130.4
.1069	61.1	63.8
.1810	97.2	105.0
.1795	95.1	102.0
.1216	65.7	68.8

The composition of the residue, which has been represented as KAs, is open to question. It might be considered as K_3As_3 ,⁹ a mixture of K_3As and metallic arsenic or a mixture of several polyarsenides of potassium. Some information regarding this question might be obtained by treating the KAs residue with ammonium bromide and also with methyl chloride in liquid ammonia solution. Such a study is now being undertaken.

(7) Dehn, *Am. Chem. J.*, **33**, 107 (1905).

(8) Stock, *Ber.*, **50**, 156 (1917).

(9) Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **154**, 1 (1931).

Summary

Arsine reacts with sodium, potassium and potassium amide in liquid ammonia to form the corresponding alkali metal dihydrogen arsenide.

Arsine is regenerated from the dihydrogen arsenide salt by ammonium bromide in liquid ammonia.

Methyl chloride reacts with potassium dihydrogen arsenide in liquid ammonia to produce methylarsine. Some of the physical properties of methylarsine have been determined.

Potassium dihydrogen arsenide decomposes at temperatures in excess of 115° to produce hydrogen and a polyarsenide of potassium.

